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(71)Applicant : MITSUBISHI CHEM CORP

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(72)Inventor : KINOSHITA SHINICHI
OKAHARA KENJI

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve safety of a nonaqueous electrolyte secondary battery.

SOLUTION: This battery is composed of at least a positive electrode active material, a negative electrode active material, a separator and a nonaqueous electrolyte. In this case, components of the following (a), (b), (c) and (d) are contained in this nonaqueous electrolyte, and a flash point of this nonaqueous electrolyte measured by a tag type flash point measuring test in accordance with JIS-K 2810 is set not less than 50°C.

(a) A high dielectric constant solvent not less than a specific dielectric constant 50, (b) A low viscosity solvent whose viscosity at 25°C is not more than 1 centipoise, (c) fluorine type alkane or fluorine-contained ether and (d) an electrolyte are contained.

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CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by being a positive active material, a negative-electrode active material, separator, and the nonaqueous electrolyte rechargeable battery that consists of nonaqueous electrolyte, and the flash point of this nonaqueous electrolyte measured by the tag formula flash point measurement examination which the aforementioned nonaqueous electrolyte contains (a), (b), (following c), and following (d) component, and is based on JIS-K2810 being 50 degrees C or more.
 (a) 50 or more specific inductive capacity -- high -- the viscosity in dielectric constant (solvent b) 25 degree C -- the hypoviscosity solvent (c) molecular formula (I) of 1 or less centipoise
 $CpHqNrOsFt(I)$

(-- for 4-10q, 0-21r are [p / 0-6, and t of 0-4s] the number of 1-22 among a formula ** fluorine organic-solvent (d) electrolyte expressed with).

[Claim 2] (c) The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by the vapor pressure in 25 degrees C of the ** fluorine organic solvent of a component being 25 - 760mmHg.

[Claim 3] (c) the ** fluorine organic solvent expressed with the formula (I) of a component -- C5 F12 and C6 -- F14 and C -- seven F16, C8 F18, 2 (CF3) CH-CF2 OCH3, CF3 CF2 CH2 OCF2 CF2 H, and CF3 3 (CF2) OCH3
 Nonaqueous electrolyte rechargeable battery according to claim 1 which is the selected solvent.

[Claim 4] (c) The ** fluorine organic solvent of a component is a nonaqueous electrolyte rechargeable battery according to claim 1 characterized by containing 0.5 to 30% of the weight among nonaqueous electrolyte.

[Claim 5] (d) the high dielectric constant solvent of a component is chosen from ethylene carbonate and propylene carbonate, and the hypoviscosity solvent of the (b) component chooses out of 1, 2-dimethoxyethane, diethyl carbonate, dimethyl carbonate, and ethyl methyl carbonate -- having -- both mixing ratio -- a:b -- a capacity factor -- 1:3-8:1 -- the nonaqueous electrolyte rechargeable battery according to claim 1 characterized by a certain thing

[Claim 6] The nonaqueous electrolyte rechargeable battery according to claim 1 whose electrolyte is lithium salt chosen from LiClO4, LiAsF6, LiPF6, LiBF4, LiB (C6 H5)4, LiCl, LiBr, CH3 SO3 Li, and CF3 SO3 Li.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the new nonaqueous electrolyte rechargeable battery which was excellent in the safety which has fire retardancy, and was moreover excellent in the low-temperature property. Especially this thing is useful on the cell for electric vehicles.

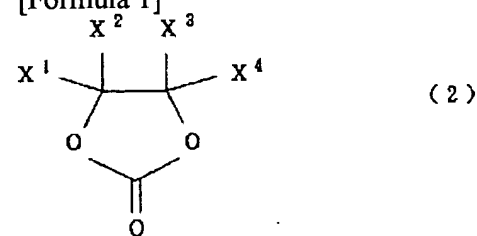
[0002]

[Description of the Prior Art] Since it has a high voltage and high-energy density and excels in keeping, the rechargeable battery using nonaqueous electrolyte is widely used in recent years as a power supply of consumer electronics, such as a handicap video camera and a portable personal computer. As a non-aqueous solvent which constitutes the nonaqueous electrolyte of this nonaqueous electrolyte rechargeable battery, the mixed solvent of the propylene carbonate (PC) which is a high dielectric constant solvent, 1 which is a hypoviscosity solvent, 2-dimethoxyethane (DME), 2-methyl tetrahydrofuran (2-MeTHF), dimethyl carbonate (DMC), methylethyl carbonate (MEC), diethyl carbonate (DEC), etc., etc. has high conductivity, and is proposed as a solvent which can raise a cycle property.

[0003] However, even if it uses the solvent of the above propylene carbonate systems, it is pointed out to JP,7-240232,A that the cycle property of a lithium secondary battery cannot fully be raised. Furthermore, the electric vehicle attracts attention from the environmental problem etc., and although it is proposed that an energy density uses a maintenance-free nonaqueous electrolyte rechargeable battery for electric vehicles with closed mold highly, generally as for a hypoviscosity solvent, for a low reason, the flash point has the danger of ignition. By the large-sized cell for electric vehicles, since there is little thermolysis, elevation of the interior temperature of a cell is large at the time of a surcharge or a short circuit, and tends [especially] to cause rupture of the cell by elevation of the internal pressure by decomposition and evaporation of the electrolytic solution and the outflow of the electrolytic solution, and ignition at it.

[0004] As a nonaqueous electrolyte rechargeable battery which improved the cycle property, for JP,7-240232,A, it sets to a nonaqueous electrolyte rechargeable battery equipped with the negative electrode which consists a lithium of a dope, the material which can carry out a ** dope, a metal lithium, or a lithium alloy, a positive electrode, and the nonaqueous electrolyte by which the electrolyte is dissolved in the non-aqueous solvent, and a non-aqueous solvent is the following formula [0005].

[Formula 1]



[0006] (-- at least one of X₁, X₂, X₃, and the X₄ expresses F, Cl, or Br among a formula The coin type nonaqueous electrolyte rechargeable battery characterized by including the annular carbonate expressed with) is proposed. Moreover, JP,8-37024,A is a rechargeable battery which considers a positive electrode, a negative electrode, and the organic electrolytic solution as basic composition, and proposes the nonaqueous electrolyte rechargeable battery with which this organic electrolytic solution is characterized by containing the ** fluorine ether.

[0007] Although a cycle property is improved, since offer of a small rechargeable battery which was excellent in the

low-temperature property makes the purpose the rechargeable battery indicated by these official reports, examination is not made about fire retardancy like the cell of an electric vehicle.

[0008]

[Problem(s) to be Solved by the Invention] this invention aims at offer of a nonaqueous electrolyte rechargeable battery which was excellent in safety since there was no danger of ignition or ignition, and was moreover excellent in the low-temperature property.

[0009]

[Means for Solving the Problem] This inventions are a positive active material, a negative-electrode active material, separator, and a nonaqueous electrolyte rechargeable battery that consists of nonaqueous electrolyte, and offer the nonaqueous electrolyte rechargeable battery characterized by the flash point of this nonaqueous electrolyte measured by the tag formula flash point measurement examination which the aforementioned nonaqueous electrolyte contains (a), (b), (following c), and following (d) component, and is based on JIS-K2810 being 50 degrees C or more.

[0010] (a) 50 or more specific inductive capacity -- high -- the viscosity in dielectric constant (solvent b) 25 degree C -- the hypoviscosity solvent (c) molecular formula (I) of 1 or less centipoise

CpHqNrOsFt (I)

(-- for 4-10q, 0-21r are [p / 0-6, and t of 0-4s] the number of 1-22 among a formula ** fluorine organic-solvent (d) electrolyte expressed with).

[0011]

[Function] The safety of a cell can be raised without being able to make into 50 degrees C or more the flash point of the nonaqueous electrolyte measured by the tag formula flash point measurement examination which the mixed solvent of a high dielectric constant solvent and a hypoviscosity solvent is made to carry out the amount content of specification of the ** fluorine organic solvent further, and is based on it as a solvent in nonaqueous electrolyte at JIS-K2810, and spoiling the conventional cell performance.

[0012]

[Embodiments of the Invention] Hereafter, this invention is explained in detail.

Structure of a nonaqueous-electrolyte rechargeable battery: The structure of a nonaqueous electrolyte rechargeable battery is a tubed type cell as shown in drawing 1. the inside of drawing, and 1 -- a positive electrode and 2 -- a negative electrode and 3 -- for separator and 6, as for a cell obturation board and 8, packing, and 9 and 10 are [a positive-electrode lead terminal and 4 / a negative-electrode lead terminal and 5 / a cell container and 7] electric insulating plates

[0013] Negative electrode: As a negative-electrode active material, although you may be a lithium and a lithium alloy, occlusion and the carbon material which can be emitted are desirable in a lithium with more high safety. Although especially this carbon material is not limited, carbon material which graphitized a part of these, such as carbide, such as the carbide of a graphite and coal system corks, petroleum system corks, and a petroleum system pitch, carbide of a petroleum system pitch, a needle coke, pitch coke, phenol resin, and a crystalline cellulose, furnace black, acetylene black, a pitch based carbon fiber, etc. are mentioned. A negative electrode applies that which slurred the negative-electrode active material and the binder (binder) with the solvent, dries and is used as a sheet-like object.

[0014] positive-electrode: -- a positive active material -- a lithium -- occlusion or the metallic-oxide system compound which can carry out an intercalation, a cull scorch night system compound, etc. -- desirable -- LixCoO2, LixMnO2, LixMn 2O4, LixV 2O3, and LixTiS2 etc. -- it is mentioned What the positive electrode applied that which slurred the positive active material, the binder (binder), and the electric conduction agent with the solvent, and was dried and was used as the sheet-like object is used.

[0015] As a binder (binder) of a negative-electrode active material or a positive active material, a polyvinylidene fluoride, a polytetrafluoroethylene, EPDM (ethylene-propylene-diene ternary polymerization object), SBR (styrene butadiene rubber) and NBR (acrylonitrile-butadiene rubber), a fluororubber, etc. are hung up, for example. As an electric conduction agent of a positive electrode, although the particle of amorphous carbon, such as carbon black, such as a particle of a graphite and acetylene black, and a needle coke, etc. is used, it is not limited to these.

[0016] The organic solvent which usually dissolves a binder is used as a solvent which slurs. For example, N-methyl pyrrolidone, a dimethylformamide, a dimethylacetamide, a methyl ethyl ketone, a cyclohexanone, methyl acetate, a methyl acrylate, diethyl triamine, N-N-dimethylamino propylamine, ethylene oxide, a tetrahydrofuran, etc. can be hung up. Moreover, a dispersant, a thickener, etc. may be added to water and an active material may be slurred by latexes, such as SBR. When using the charge collector of a negative electrode, copper, nickel, stainless steel, nickel-plating steel, etc. are used, and when using a positive-electrode charge collector, aluminum, stainless steel, nickel-plating steel, etc. are used.

[0017] Separator: The high polymer film of fine porosity is used as separator, and the object which consists of polyolefine system macromolecules, such as polyamides, such as nylon 6 and Nylon 66, a cellulose acetate, a nitrocellulose, a polysulfone, a polyacrylonitrile, a polyvinylidene fluoride, and polypropylene, polyethylene, a polybutene, is used. It is a factor with electrochemistry stability important chemically [separator]. This point to a polyolefine system macromolecule is desirable, and it is desirable that it is a product made from polyethylene from the point of the self-lock out temperature which is one of the purposes of a battery separator.

[0018] in the case of the separator made from polyethylene, it is ultra high molecular weight polyethylene from the point of elevated-temperature configuration maintenance nature -- desirable -- the minimum of the molecular weight -- desirable -- 500,000 -- further -- desirable -- 1 million -- it is 1,500,000 most preferably the upper limit of another side molecular weight -- desirable -- 5 million -- further -- desirable -- 4 million -- it is 3 million most preferably It is because it elapses, and the hole of separator may not blockade when [that a fluidity is low] heated, if molecular weight is too large.

[0019] Nonaqueous electrolyte: For the nonaqueous electrolyte used by this invention, the viscosity in with a (a) specific inductive capacity of 50 or more quantity dielectric constant (solvent b) 25 degree C is the hypoviscosity solvent (c) molecular formula (I) of 1 or less centipoise.

CpHqNrOsFt (I)

(-- for 4-10q, 0-21r are [p / 0-6, and t of 0-4s] the number of 1-22 among a formula The flash point of this nonaqueous electrolyte measured by the tag formula flash point measurement examination which contains the ** fluorine organic-solvent (d) electrolyte expressed with), and is based on JIS-K2810 is a thing 50 degrees C or more.

[0020] (a) High dielectric constant solvent : as a with a specific inductive capacity of 50 or more high dielectric constant solvent contained in the nonaqueous electrolyte of this invention, it is desirable to use propylene carbonate (PC), ethylene carbonate (EC), or these mixed solvents, for example. This high dielectric constant solvent is preferably contained 40 to 60% of the weight 20 to 80% of the weight among nonaqueous electrolyte.

[0021] (b) Hypoviscosity solvent : the viscosity (Brookfield viscosity) in 25 degrees C can use 1, 2-dimethoxyethane (DME), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), or these two or more sorts of mixed solvents as a hypoviscosity solvent of 1 or less centipoise.

[0022] If the viscosity in 23 degrees C exceeds 1 centipoise, the cycle property of a rechargeable battery is low, and the capacity of a cell becomes low when current density of a rechargeable battery is made high.

(a) the rate (a:b) of a volume ratio of (b) hypoviscosity solvent to a high dielectric constant solvent -- 1:3-8:1 -- it is 1:4-2:1 preferably Since an electrolytic degree of dissociation will fall and electrical conductivity will fall if there are more hypoviscosity solvents than this ratio, a desired cell property is not not discovered and desirable. A hypoviscosity solvent is preferably contained 30 to 50% of the weight ten to 60% of the weight among nonaqueous electrolyte.

[0023] (c) ** fluorine organic-solvent: -- although what dissolved the electrolyte in the mixed solvent of the above-mentioned quantity dielectric constant solvent and a hypoviscosity solvent is usually used for the electrolytic solution -- especially -- the flash point of a hypoviscosity solvent -- a low sake -- the electrolytic solution -- a cell container to a certain factor -- jet -- the bottom -- a case -- ignition -- it is dangerous Then, in this invention, without spoiling the performance of a cell by mixing the ** fluorine organic solvent shown by the stable aforementioned formula (I) electrochemically and chemically in the electrolytic solution by self-incombustibility, the flash point of the electrolytic solution is pulled up and the safety of a cell is raised.

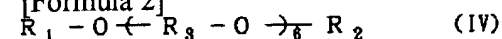
[0024] As this ** fluorine organic solvent, it is a formula (III).

F(CF₂)_aF (III)

(-- a is the number of 5-8 among a formula The fluorine system alkane shown by), and formula (IV)

[0025]

[Formula 2]



[0026] each is the same although R₁, R₂, and R₃ express a fluorine substitution hydrocarbon group univalent [of the straight chain containing a hydrocarbon group univalent / of the straight chain of C₁-C₆, or branching /, or divalent, or one or more fluorine atoms, or branching], or divalent among a formula -- or you may differ R₁, R₂, and R₃ One or more fluorine atoms are included in at least one. b is the number of 0-8. The ** fluorine chain-like ether compound shown is mentioned.

[0027] That C₅ F₁₂, C₆ F₁₄, C₇ F₁₆, and C₈ F₁₈ are indicated to be by the following formula as a ** fluorine chain-like ether compound shown by the formula (IV) as a fluorine system alkane shown by the formula (III), for example can be used.

[0028]

[Formula 3] $2 \text{ CHCF}_2 \text{ OCH}_3$ and $\text{CF}_3 \text{ CFHCF}_2 \text{ OCH}_3$, $(\text{CF}_3) \text{ CF}_3 \text{ CF}_2 \text{ CH}_2 \text{ OCF}_2 \text{ CF}_2 \text{ H}$ and $\text{HCF}_2 \text{ CF}_2 \text{ OCH}_3$, $\text{HCF}_2 \text{ CF}_2 \text{ OC}$ two H 's and $\text{CF}_3 \text{ CH}_2 \text{ OCH}_2 \text{ CF}_3$, $\text{C}_4 \text{H}_9 \text{ OCF}_2 \text{ CF}_2 \text{ H}$ and $\text{F}(\text{CF}_2)_3 \text{ CH}_2 \text{ NH}_2$, $\text{F}(\text{CF}_2)_7 \text{ CH}_2 \text{ NH}_2$ and $\text{CF}_3 \text{ C}_2 \text{ OCHF}_2$, $\text{C}_3 \text{ F}_7 \text{ OCHF}_2$, $2 (\text{CF}_3) \text{ CHOCH}_2 \text{ F}$, $\text{F} [\text{CF}(\text{CF}_3) \text{ CF}_2 \text{ O}]_2 \text{ CHFCF}_3$ and $2 (\text{CF}_3) \text{ CFOCH}_2 \text{ CH}=\text{CH}_2$, $\text{CF}_3 \text{ 2 } (\text{CF}_2) \text{ CH}_2 \text{ OCH}_2 \text{ CH}=\text{CH}_2$ and $\text{CF}_3 \text{ 6 } (\text{CF}_2) \text{ CH}_2 \text{ OCH}_2 \text{ CH}=\text{CH}_2$, $\text{CF}_3 \text{ CHFCF}_2 \text{ OCH}_2 \text{ CH}=\text{CH}_2$, $\text{CHF}_2 \text{ CF}_2 \text{ OCH}_2 \text{ CH}=\text{CH}_2$, and $\text{CF}_3 \text{ CH}_2 \text{ OCF}=\text{CF}_2$, $\text{CF}_3 \text{ CH}_2 \text{ OCH}=\text{CH}_2$, $\text{CF}_3 \text{ OCF}=\text{CF}_2$, and $\text{CH}_3 \text{ O} [\text{CH}(\text{CF}_3) \text{ CH}_2 \text{ O}]_n \text{ CH}_3$ ($n=1-7$)

[0029] Fluorine system ARUAN of a liquid is desirable at 25 degrees C also in these. The vapor pressure in 25 degrees C of this ** fluorine organic solvent is 70 - 500mmHg 50 to 600 mmHg 25 to 760 mmHg preferably. When vapor pressure is too high, there is a possibility that the internal pressure of a cell may rise and explode.

[0030] The ** fluorine organic solvent of this (c) component is preferably contained five to 30% of the weight 0.5 to 30% of the weight among nonaqueous electrolyte. When there are few content rates of this (c) component, the improvement effect of nonflammable-izing of a rechargeable battery is inferior. Moreover, if many [conversely], electrical conductivity will fall and a desired cell property will not be discovered.

[0031] (d) Electrolyte : as an electrolyte, it is independent about LiClO_4 , LiAs F_6 , $\text{LiCF}_3 \text{ SO}_3$, $\text{LiCF}_3 \text{ CHFCF}_2 \text{ SO}_3$, $\text{LiCF}_2 \text{ HCF}_2 \text{ SO}_3$, $\text{LiCF}_2 \text{ HSO}_3$, LiBF_4 , LiPF_6 , $\text{Li}(\text{CF}_3 \text{ SO}_2)_2 \text{ N}$, etc., or plurality can be mixed, and it can dissolve and use for the above-mentioned solvent. The electrolyte concentration in the electrolytic solution has the most desirable range of 0.5 - 2.0 mol concentration. Even if this value is too small and it is too large, the electric **** of a solution falls and a desired cell property is not not discovered and desirable.

[0032] The flash point of nonaqueous electrolyte: Although it is desired for the flash point of the electrolytic solution to be more high, when **, the cell room air temperature of an electric vehicle, etc. are considered among the devices in the case of using as a power supply of consumer electronics, 50 degrees C or more of flash points measured by the tag formula flash point measurement examination based on JIS-K2810 are 55-400 degrees C preferably.

[0033] As for the nonaqueous electrolyte rechargeable battery of this invention, it is effective to apply to the large-sized cell which exists in the large quantity of nonaqueous electrolyte. The object for electric vehicles, and since there is little thermolysis by the large-sized cell for [night] power storage, elevation of the interior temperature of a cell is large at the time of a surcharge or a short circuit, and tends [especially] to cause rupture of the cell by elevation of the internal pressure by decomposition and evaporation of the electrolytic solution and the outflow of nonaqueous electrolyte, and ignition at it. Under the present circumstances, since it is possible that the electrolytic solution ignites by a certain cause, it becomes very important on [of a cell] safe to make the flash point of nonaqueous electrolyte high.

[0034]

[Example] Although an example is given and this invention is hereafter explained further to a detail, this invention is not limited by the following examples unless the summary is exceeded. In addition, the evaluation method in an example is as follows. That it is with the "section" shows the "weight section" among an example and the example of comparison.

[0035] (Manufacture of a negative electrode) the coal system needle-coke 90 section (weight rate; especially when there is no description, it is the same as that of the following) of 10 micrometers of mean particle diameters -- N-methyl pyrrolidone solution (2 % of the weight) of the polyvinylidene-fluoride 10 section -- mixing -- a negative electrode -- a mixture -- it considered as the slurry It applied to both sides of the copper foil of 20-micrometer thickness, and it dried, the solvent was evaporated, roll processing was carried out, and the negative electrode was produced.

[0036] a negative electrode -- the size of the application section of a mixture was made to 12cmx15cm, and thickness was made into 250 micrometers of one side right and left of copper foil -- the left -- 25mm and the right -- a 15mm ear - - leaving -- a negative electrode -- it has designed so that a mixture may be applied in addition, the electrode which constitutes the edge of a cell -- a negative electrode -- a mixture is applied only to one side

[0037] (Manufacture of a positive electrode) the thing 90 section which carried out preferential grinding with the ball mill again and which was heat-treated in 5-hour air at 850 more degrees C after carrying out preferential grinding of the two mols of the cobalt carbonate to one mol of lithium carbonates with the ball mill and heat-treating in 5-hour air at 850 degrees C -- as an electric conduction agent -- acetylene black -- the five sections, in addition the mixed thing -- N-methyl pyrrolidone solution (2 % of the weight) of the polyvinylidene-fluoride 5 section -- mixing -- a positive electrode -- a mixture -- it considered It applied to both sides of the aluminum foil of 25-micrometer thickness, and it dried, the solvent was evaporated, roll processing was carried out, and the positive electrode was created.

[0038] a positive electrode -- the size of the application section of a mixture was made to 12cmx15cm, and thickness was made into 250 micrometers of one side right and left of an aluminum foil -- the right -- 25mm and the left -- a 15mm ear -- leaving -- a positive electrode -- it has designed so that a mixture may be applied in addition, the electrode

which constitutes the edge of a cell -- a positive electrode -- a mixture is applied only to one side

[0039] (Manufacture of separator) In 135 degrees C of melting points, it is molecular weight (viscosity average) 2×10^6 .

After extruding in the shape of a film from a T die continuously, having supplied the ultra-high-molecular-weight-polyethylene powder 20 section and the ceryl-alcohol 80 section to the extruder, and kneading at 230 degrees C, melting deformation was added in the direction of a machine, and the film of 50 micrometers of thickness was obtained. The obtained film was immersed into 80-degree C isopropyl alcohol, extraction removal of the ceryl alcohol was carried out out of the film, subsequently, it heat-treated for 30 seconds in the heating pinch roll of 125 degrees C of skin temperatures, and the porous film of 25-micrometer thickness was obtained.

[0040] (Assembly of a cell) The laminating of the above-mentioned negative electrode and the positive electrode was carried out through separator by turns, and the cell was assembled. that time -- the electrode of ends -- an electrode -- that to which only one side applied the mixture was used In a negative electrode and a positive electrode, a metal rod is welded separately, respectively and the charge collector to which the negative electrode and the positive electrode were connected electrically respectively separately is formed.

[0041] in addition, the direction which carries out the laminating of the cell -- the frame of a non-conductor -- with, it bound tight when the laminating of the half (the electrode of ends -- one side -- an electrode -- it becomes half since the mixture is applied) was carried out for the electrode of the above-mentioned size to 26 sets, the cell 12 which has the charge-and-discharge capacity of about 350 Whs was produced

[0042] (Assembly of a group cell) After carrying out the vacuum deairing of the above-mentioned cell 12 by 1×10 to 2 or less Torrs, it supplied in the dry box replaced by Ar gas. As shown in drawing 2, the ten above-mentioned cells were contained in the container 6 equipped with the septum made from polypropylene, nonaqueous electrolyte 11 was poured in, and the top cover 7 was shut. At this time, the top cover was penetrated and the negative-electrode terminal of each cell and the terminal of a positive electrode considered as the form projected in the upper part of a container. This terminal was closed by the suitable encapsulant in the penetration portion of a top cover. The hole with a diameter of 10mm was made in the container upper part made from polypropylene at this time.

[0043] As nonaqueous electrolyte used for the example 1 above-mentioned group cell, the rate of the ethylene carbonate (160 degrees C of flash points) of a high dielectric constant solvent, and 1 of a hypoviscosity solvent and 2-dimethoxyethane (1 degree C of flash points) blended with the mixed-solvent 85 section of 1:1 fluorine system alkane C6 F14 [15-section] (with no flash point) which is a ** fluorine organic solvent, the hexafluoro phosphoric-acid lithium salt (LiPF6) which is an electrolyte further was dissolved in one mol/l, and nonaqueous electrolyte was

[0044] When the flash point was measured by the tag formula flash point measurement examination based on JIS-K2810 in this nonaqueous electrolyte, it was 60 degrees C. A rechargeable battery is the bottom of 25-degree-C atmosphere, and 1 mA/cm². After charging until the cell voltage amounted to 4.2V by constant-current density, the hole of the container upper part was covered with the rubber stopper which applied adhesives.

[0045] (The short-circuit test and the inflammable test of a group cell) When the above-mentioned group cell was short-circuited with copper wire and between the bottom of 25-degree-C atmosphere, the positive-electrode terminal, and the negative-electrode terminal was kept, there was no deformation of a cell. Moreover, although the ignition source was beforehand held up to the position of 10cm of upper parts of a hole and the inflammable test was performed, it did not ignite to the electrolytic solution, therefore did not result in combustion of a cell. Although the evaluation temperature of 25 degrees C of a rechargeable battery was changed with 40 degrees C and 50 degrees C and inflammability was evaluated, neither ignited. A result is collectively shown in Table 1.

[0046] As example of comparison 1 nonaqueous electrolyte, the rate of the ethylene carbonate of a high dielectric constant solvent, and 1 of a hypoviscosity solvent and 2-dimethoxyethane used for the mixed solvent of 1:1 what dissolved the hexafluoro phosphoric-acid lithium salt (LiPF6) which is an electrolyte in one mol/l., and also it evaluated like the example 1.

[0047] The flash point of nonaqueous electrolyte was 5 degrees C. When between the bottom of 25-degree-C atmosphere, the positive-electrode terminal, and the negative-electrode terminal was short-circuited with copper wire, while the cell blistered after a while, the rubber stopper of the hole of the container upper part separated from this group cell, and the electrolytic solution blew off. Beforehand, when the ignition source was held up to the position of 10cm of upper parts of a hole, the electrolytic solution ignites and the cell came to burn. The result which changed the temperature on which a cell is put similarly with 40 degrees C and 50 degrees C, and evaluated it hereafter is collectively shown in Table 1.

[0048] As nonaqueous electrolyte used for a 2 sets of examples cell, the ** fluorine ether (CF₃)₂ and CH₃-C₂OCH₃ 20 (with no flash point) section was blended with the mixed-solvent 80 section of 1:1, and the rate of the ethylene carbonate of a high dielectric constant solvent, and 1 of a hypoviscosity solvent and 2-dimethoxyethane dissolved the

hexafluoro phosphoric-acid lithium salt (LiPF₆) which is an electrolyte further in one mol/l., and prepared nonaqueous electrolyte.

[0049] When the flash point was measured by the tag formula flash point measurement examination based on JIS-K2810 in this nonaqueous electrolyte, it was 55 degrees C. Like the example 1, under 25-degree-C atmosphere, although the short-circuit test and the inflammable test of a cell were performed, it did not ignite to the electrolytic solution, therefore did not result in combustion of a cell.

[0050]

[Table 1]

表1 電池の安全性評価結果

評価温度	実施例 1	実施例 2	比較例 1
25℃	○	○	×
40℃	○	○	×
50℃	○	○	×

O: with no ignition. x: Those with ignition.

[0051] In addition, the cell property (cycle nature) of the assembly cell of an example 1, an example 2, and the example 1 of comparison was equivalent.

[0052]

[Effect of the Invention] The nonaqueous electrolyte rechargeable battery of this invention has improved the safety remarkably, without spoiling a cell property.

[Translation done.]